PTO 08-1131

CC = JP
20010130
Kokai
13026658

2001-026658

POLYLACTIC ACID-TYPE RESIN COMPOSITION AND THE METHOD OF ITS MANUFACTURE

[Porinyusankei jushisoseibutsu oyobi sono seizohoho]

Yasunori Yoshida et al.

UNITED STATES PATENT NO. AND TRADEMARK OFFICE
WASHINGTON, D.C. DECEMBER 2007
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	13026658
DOCUMENT KIND	(12):	Kokai
PUBLICATION DATE	(43):	20010130
APPLICATION NUMBER	(21):	11199090
APPLICATION DATE	(22):	19990713
INTERNATIONAL CLASSIFICATION[7]	(51):	C 08 J 5/18
		B 32 B 27/36
		C 08 G 63/91
		C 08 K 5/14
		C 08 L 67/04
INVENTORS	(72):	Yasunori Yoshida et al.
APPLICANT	(71):	Mitsui Chemicals, Inc.
TITLE	(54):	POLYLACTIC ACID-TYPE RESIN COMPOSITION AND THE METHOD OF ITS MANUFACTURE
FOREIGN TITLE	[54A]:	Porinyusankei jushisoseibutsu oyobi sono seizohoho

Claims /2*

1. A polylactic acid-type resin composition, being a polylactic acid-type resin composition obtained by melt kneading a resin component [Ingredient (A)] that includes polylactic acid [Ingredient (a-1)] and aliphatic polyester [Ingredient (a-2)], and an organic peroxide component [Ingredient (B)] within a temperature range of 150-250°C; characterized by the fact, that the composition ratio of polylactic acid [Ingredient (a-1)], aliphatic polyester [Ingredient (a-2)], and organic peroxide component [Ingredient (B)], based upon polylactic acid [Ingredient (a-1)] being 100 parts by weight, is 10-300 parts by weight of aliphatic polyester [Ingredient (a-2)], 0.01-5 parts by weight of organic peroxide component [Ingredient (B)]; and the polylactic acid [Ingredient (a-1)] has a weight average molecular weight Mw of 30,000-500,000, the aliphatic polyester [Ingredient (a-2)] has a weight average molecular weight Mw of 30,000-500,000, an elastic modulus of 50-1000 MPa, and an elongation of 20-2000%.

2. The polylactic acid-type resin composition according to Claim 1, wherein the aliphatic polyester [Ingredient (a-2)] is at least 1 selected from the group comprising copolymers of hydroxyvaleric acid and hydroxybutyric acid, and polycaprolactone, polybutylene succinate, and polyethylene succinate.

3. The polylactic acid-type resin composition according to Claim 1 or Claim 2, wherein (1) the melt tension at a melt flow index of 10 [g/10 min] is 0.7-20 [g], (2) elastic modulus is 50-1500 [MPa], and (1) [sic] elongation is 100-2000 [%].

4. A method for manufacturing a polylactic acid-type resin composition, being a polylactic acid-type resin composition obtained by melt kneading a resin component [Ingredient (A)] that includes polylactic acid [Ingredient (a-1)] and aliphatic polyester [Ingredient (a-2)], and an organic peroxide component [Ingredient (B)] within a temperature range of 150-250°; characterized by the fact that the composition ratio of polylactic acid [Ingredient (a-1)], aliphatic polyester [Ingredient (a-2)], and organic peroxide component [Ingredient (B)], based upon polylactic acid [Ingredient (a-1)] being 100 parts by weight, is

* [Numbers in right margin indicate pagination of the original text.]

10-100 parts by weight of aliphatic polyester [Ingredient (a-2)], 0.01-5 parts by weight of organic peroxide component [Ingredient (B)]; and the polylactic acid [Ingredient (a-1)] has a weight average molecular weight Mw of 30,000-500,000, the aliphatic polyester [Ingredient (a-2)] has a weight average molecular weight Mw of 30,000-500,000, an elastic modulus of 50-1000 MPa, and an elongation of 20-2000%.

5. The method for manufacturing a polylactic acid-type resin composition according to Claim 4, wherein the aliphatic polyester [Ingredient (a-2)] is at least 1 selected from the group comprising copolymers of hydroxyvaleric acid and hydroxybutyric acid, and polycaprolactone, polybutylene succinate, and polyethylene succinate.

6. The method for manufacturing a polylactic acid-type resin composition according to Claim 4 or Claim 5, wherein (1) the melt tension at a melt flow index of 10 [g/10 min] is 0.7-20 [g], (2) elastic modulus is 50-1500 [MPa], and (3) elongation is 100-2000 [%].

7. A molded article containing the polylactic acid-type resin composition described in any of Claims 1-3.

8. A film containing the polylactic acid-type resin composition described in any of Claims 1-3.

9. An inflation film containing the polylactic acid-type resin composition described in any of Claims 1-3.

10. A foam containing the polylactic acid-type resin composition described in any of Claims 1-3.

11. A laminate containing a resin layer and a substrate layer, wherein the aforementioned resin layer contains the polylactic acid-type resin composition described in any of Claims 1-3.

12. A paper laminate product containing a resin layer and a paper layer, and where the aforementioned resin layer contains the polylactic acid-type resin composition described in any of Claims 1-3.

13. An aluminum laminate product containing a resin layer and an aluminum layer, and where the aforementioned resin layer contains the polylactic acid-type resin composition described in any of Claims 1-3.

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention pertains to a polylactic acid-type resin composition. It also pertains to a method for obtaining the polylactic acid-type resin composition.

[0002]

Prior art

Generally, resins that have excellent flexibility, thermal resistance, and water resistance are as follows: polyethylene, polypropylene, soft polyvinyl chloride, and polyethylene terephthalate, for example; they are used in various fields that take advantage of properties such as light weight, heat /3
insulating properties, soundproofing, and cushioning properties. Nevertheless, the recovery and reuse of these resins after use is difficult, and since they are more or less nonbiodegradable, they remain semipermanently in the earth. When discarded, they cause other problems such as spoiling the scenery and destroying the living environment of marine life.

[0003]

As a countermeasure, aliphatic polyesters have been developed that are derived from aliphatic polyhydric alcohol and aliphatic polyvalent carboxylic acid, and lactic acid-type polymers such as

copolymers of polylactic acid and lactic acid with other aliphatic hydroxycarboxylic acids. Among these polymers are some that are 100% biodegradable after several months, or at least before 1 year has passed, within the body of an animal, or if placed in the soil or seawater, will begin degrading within several weeks in a moist environment, and disappear after about 1 or several years. As biodegradable objects, they have the advantage of becoming lactic acid, carbon dioxide, and water, which are harmless to the human body.

[0004]

In particular, recent years that promise an enlargement of the field of application; it has become possible to manufacture polylactic acid in large amounts inexpensively by fermentation with L-lactic acid as the raw material; it has excellent properties such as that of degrading rapidly in compost, and it resists causing odorization and discoloration of food products, for example. Nevertheless, because polylactic acid is very rigid it cannot be easily said to be a suitable resin for applications that require flexibility such as films and wrapping materials; thus a technology is known for softening it by blending with other biodegradable resins. Examples of such resins include polybutylene succinate, polyethylene succinate, and polycaprolatone, and descriptions are given in Japanese Kokai Patent Applications No. Hei 8[1996]-245866 and Hei 9[1997]-111107.

[0005]

However, although softening is possible with a simple blend (specifically, it is possible to lower the elastic modulus), there is almost no improvement in elongation, and the defects of being easily cut and broken remain. Also, since polylactic acid generally has low melt tension, the problem remains of it being inadequate for molding methods such as inflation molding and lamination molding. In other words,

because there is insufficient melt tension during melt molding, there are problems of large neck-in and of breaks occurring easily during molding.

[0006]

The idea of causing fine cross-linkage of polymers has been conceived as a method for improving the melt tension. The method of using an organic peroxide is a method for causing fine cross-linkage of polymers. WO 95/18169 (Japanese Tokuhyo Patent Application No. Hei 10[1998]-501560) and U.S. Patent No. 5594095 of the reaction extrusion of an organic peroxide against polylactic acid. Nevertheless, even causing fine cross-linkage using an organic peroxide against polylactic acid, although it improves the melt tension, cannot accomplish the object of the present invention because rigidity and elastic modulus are intrinsically high, and elongation is also unimproved.

[0007]

The method in which plasticizer is added to bring about flexibility has the problem of bleed-out, depending on the type and amount, and cannot be said to be a satisfactory method for all applications. Therefore the current situation is one in which a technology has yet to be discovered whereby the flexibility of polylactic acid can be improved while at the same time improving the melt tension.

[0008]

Problem to be solved by the invention

The problem to be solved by the present invention is to offer a polylactic acid-type resin composition with improved flexibility and melt tension, and excellent mold-finishing characteristics, as well as the method of its manufacture.

[0009]

Means to solve the problem

As the result of conducting a series of diligent investigations of polylactic acid, the inventors discovered a polylactic acid-type resin composition, and the method of its manufacture, that satisfied the aforementioned object of improving elongation and melt tension by bringing about a reaction of a specific proportion of polylactic acid, aliphatic polyester, and organic peroxide in an extruder, thus arriving at the present invention. More specifically, the present invention is detailed by the particulars described in Sections [1]-[13] below.

[0010]

[1] A polylactic acid-type resin composition obtained by melt kneading a resin component [Ingredient (A)] that includes polylactic acid [Ingredient (a-1)] and aliphatic polyester [Ingredient (a-2)], and an organic peroxide component [Ingredient (B)] within a temperature range of 150-250°C; characterized by the fact that the composition ratio of polylactic acid [Ingredient (a-1)], aliphatic polyester [Ingredient (a-2)], and organic peroxide component [Ingredient (B)], based upon polylactic acid [Ingredient (a-1)] being 100 parts by weight, is 10-300 parts by weight of aliphatic polyester [Ingredient (a-2)], 0.01-5 parts by weight of organic peroxide component [Ingredient (B)]; and the polylactic acid [Ingredient (a-1)] has a weight average molecular weight Mw of 30,000-500,000, the aliphatic polyester [Ingredient (a-2)] has a weight average molecular weight Mw of 30,000-500,000, an elastic modulus of 50-1000 MPa, and an elongation of 20-2000%.

[0011]

[2] The polylactic acid-type resin composition according to [1], wherein the aliphatic polyester [Ingredient (a-2)] is at least 1 species selected from the group comprising copolymers of hydroxyvaleric acid and hydroxybutyric acid, and polycaprolactone, polybutylene succinate, and polyethylene succinate.

[3] The polylactic acid-type resin composition according to [1] or [2], wherein (1) the melt tension at a melt flow index of 10 [g/10 min] is 0.7-20 [g], (2) elastic modulus is 50-1500 [MPa], and (2) [sic] elongation is 100-2,000 [%].

[0012]

[4] A method for manufacturing a polylactic acid-type resin composition by melt kneading a resin component [Ingredient (A)] that includes polylactic acid [Ingredient (a-1)] and aliphatic polyester [Ingredient (a-2)], and an organic peroxide component [Ingredient (B)] within a temperature range of 150-250°C; characterized by the fact that the composition ratio of polylactic acid [Ingredient (a-1)], /4
aliphatic polyester [Ingredient (a-2)], and organic peroxide component [Ingredient (B)], based upon polylactic acid [Ingredient (a-1)] being 100 parts by weight, is 10-100 parts by weight of aliphatic polyester [Ingredient (a-2)], 0.01-5 parts by weight of organic peroxide component [Ingredient (B)]; and the polylactic acid [Ingredient (a-1)] has a weight average molecular weight Mw of 30,000-500,000, the aliphatic polyester [Ingredient (a-2)] has a weight average molecular weight Mw of 30,000-500,000, an elastic modulus of 50-1000 MPa, and an elongation of 20-2000%.

[0013]

[5] The method for manufacturing a polylactic acid-type resin composition according to [4], wherein the aliphatic polyester [Ingredient (a-2)] is at least 1 selected from the group comprising copolymers of hydroxyvaleric acid and hydroxybutyric acid, and polycaprolactone, polybutylene succinate, and polyethylene succinate.

[6] The method for manufacturing a polylactic acid-type resin composition according to [4] or [5], wherein (1) the melt tension at a melt flow index of 10 [g/10 min] is 0.7-20 [g], (2) elastic modulus is 50-1500 [MPa], and (3) elongation is 100-2,000 [%].

[0014]

[7] A molded article containing the polylactic acid-type resin composition described in any of [1]-[3].

[8] A film containing the polylactic acid-type resin composition described in any of [1]-[3].

[9] An inflation film containing the polylactic acid-type resin composition described in any of [1]-[3].

[0015]

[10] A foam containing the polylactic acid-type resin composition described in any of [1]-[3].

[11] A laminate containing a resin layer and a substrate layer, wherein the aforementioned resin layer contains the polylactic acid-type resin composition described in any of [1]-[3].

[12] A paper laminate product containing a resin layer and a paper layer, and where the aforementioned resin layer contains the polylactic acid-type resin composition described in any of [1]-[3].

[13] An aluminum laminate product containing a resin layer and an aluminum layer, and where the aforementioned resin layer contains the polylactic acid-type resin composition described in any of [1]-[3].

[0016]

Embodiment of the invention

The following statements explain the invention in detail.

Molecular weight of the polylactic acid

The weight average molecular weight of the polylactic acid of the present invention is in the range of 30,000-500,000, preferably 50,000-300,000, more preferably 100,000-200,000. If the molecular weight is less than 50,000, the mechanical strength may be insufficient. If it exceeds 500,000, when the cross-linking reaction proceeds, the molecular weight will become too high, and molding and processing may become problematic.

[0017]

Method for manufacturing the polylactic acid

In the present invention, specific examples of the lactic acid as the raw material for the polylactic acid include L-lactic acid, D-lactic acid, DL-lactic acid, and mixtures thereof, and it is also possible to include lactides that are cyclic dimers of lactic acid.

[0018]

The following may be mentioned as specific examples of the method for manufacturing the polylactic acid used in the present invention.

(1) A method for direct dehydration polycondensation, with lactic acid or a mixture of lactic acid and aliphatic hydroxycarboxylic acid as the raw material (for example, the manufacturing method disclosed in U.S. Patent No. 5,310,865);

(2) A ring-opening polymerization method for melt polymerization of cyclic dimers of lactic acid (lactides) (for example, the manufacturing method disclosed in U.S. Patent No. 2,758,987);

(3) A ring-opening polymerization method for melt polymerization in the presence of a catalyst of cyclic dimers of aliphatic hydroxycarboxylic acid and lactic acid, such as epsilon-caprolactone and lactide or glycolide, for example (for example, the manufacturing method disclosed in U.S. Patent No. 4,057,537);

(4) Direct dehydration polycondensation of a mixture of lactic acid, aliphatic dihydric alcohol, and aliphatic dibasic acid (for example, the manufacturing method disclosed in U.S. Patent No. 5,428,126);

[0019]

(5) A method for condensation in the presence of an organic solvent a polymer of aliphatic dibasic acid and aliphatic dihydric alcohol and polylactic acid (for example, the manufacturing method disclosed in European Patent No. 0712880 A2);

(6) A method for solid phase polymerization, with at least one part of the process, with regard to the manufacture of a polyester polymer by conducting a dehydration polycondensation reaction in the presence of a solvent of lactic acid.

Although the above may be mentioned, the manufacturing method is not limited in particular to them. It is also possible to cause polymerization by bringing together a small amount of aliphatic polyhydric alcohol such as glycerin, an aliphatic polybasic acid such as butane tetracarboxylic acid, and a polyhydric alcohol such as a polysaccharide, for example; it is also possible to increase the molecular weight using a binding agent (higher molecular chain extender) such as a diisocyanate compound, for example.

[0020]

Aliphatic polyester

In the present invention, the aliphatic polyester is a polymer that is biodegradable and can be manufactured by various combinations of aliphatic hydroxycarboxylic acid, aliphatic dihydric alcohol, and aliphatic dibasic acid. Of these, the best results are obtained for copolymers of hydroxyvaleric acid and hydroxybutyric acid, and polycaprolactone, polybutylene succinate, and polyethylene succinate. The method for manufacturing the aliphatic polyester may be the same as the methods used for manufacturing the polylactic acid, but it is not limited to these methods. That purchased commercially

may also be used, such as Celgreen (Daicel Chemical Industries), Ton (Union Carbide), Bionole (Showa Polymer), and Biopol (Monsanto), for example.

[0021]

It is also possible to cause the polymer chain of these aliphatic polyesters to be extended by a binding agent such as diisocyanate, for example. It is also possible to cause copolymerization by bringing together a small amount of aliphatic polyhydric alcohol such as glycerin, an aliphatic polybasic acid such as butane tetracarboxylic acid, and a polyhydric alcohol such as a polysaccharide, for example.

[0022]

Flexibility of the aliphatic polyester

The aliphatic polyester of the present invention must have an elastic modulus of 50-1000 MPa and an elongation of 20-2000% in the film stretching tests described below. It is preferred that the elastic modulus be 50-500 MPa; if 1000 MPa is exceeded, satisfactory flexibility will not be obtained. It is preferred that the elongation be 100-2000%, more preferably 200-2000%; if less than 20%, it will be impossible to obtain satisfactory flexibility for the invented resin composition.

[0023]

Aliphatic hydroxycarboxylic acid

Specific examples of the aliphatic hydroxycarboxylic acid are glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 3-hydroxyvaleric acid, 4-hydroxyvaleric acid, and 6-hydroxycaproic acid, for example. It is also possible to use cyclic esters of aliphatic hydroxycarboxylic acids such as glycolide, a

dimer of glycolic acid, and epsilon-caprolactone, a cyclic ester of 6-hydroxycaproic acid. These may be used either singly or as combinations of 2 or more.

[0024]

Aliphatic dihydric alcohol

Specific examples of the aliphatic dihydric alcohol are ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, 1,3-butanediol, 1,4-butanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, neopentyl glycol, polytetramethylene glycol, 1,4-cyclohexanedimethanol, and 1,4-benzenedimethanol, for example. These may be used either singly or as combinations of 2 or more.

[0025]

Aliphatic dibasic acids

Specific examples of the aliphatic dibasic acid are succinic acid, oxalic acid, malonic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecane-diacid, dodecane-diacid, phenylsuccinic acid, and 1,4-phenylene-diacetic acid, for example. These can be used either singly or in combination.

[0026]

Molecular weight of aliphatic polyester

The weight average molecular weight Mw of the aliphatic polyester of the present invention is in the range of 30,000-500,000, preferably 50,000-300,000, more preferably 100,000-200,000. If the molecular weight is less than 30,000, the mechanical strength may be insufficient. If it exceeds 500,000, when the

cross-linking reaction proceeds, the molecular weight will become too high and molding and processing may become problematic.

[0027]

Composition ratio of the higher molecular component

In the present invention, the composition ratio of polylactic acid (a-1) and aliphatic polyester (a-2) is in the range of 10-300 parts by weight, preferably 30-200 parts by weight, more preferably 50-100 parts by weight, of aliphatic polyester (a2) per 100 parts by weight of polylactic acid (a-1). If it is less than 10 parts by weight, the flexibility will be insufficient, and if it exceeds 300 parts by weight, the head resistance of the polylactic acid-type resin composition may be lost.

[0028]

Types of organic peroxides

There are no particular limitations on the organic peroxide that may be used in the present invention, but the following may be mentioned as examples: keto-peroxide type compounds, diacyl peroxide type compounds, hydroperoxide type compounds, dialkyl peroxide type compounds, peroxyketal type compounds, peroxyester type compounds, and peroxycarbonate type compounds.

[0029]

The following may be mentioned as keto-peroxide type compounds: methylethyl ketone peroxide, methylisobutyl ketone peroxide, cyclohexyanone peroxide, and methylcyclohexanone peroxide, for example. The following may be mentioned as diacyl peroxide type compounds: isobutyryl peroxide,

3,5,5-trimethylhexanoyl peroxide, lauroyl peroxide, benzoyl peroxide, and p-chlorobenzoyl peroxide, for example.

[0030]

The following may be mentioned as hydroperoxide type compounds: t-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, p-menthane hydroperoxide, and 1,1,3,3-tetramethylbutyl hydroperoxide, for example.

[0031]

The following may be mentioned as dialkyl peroxide type compounds: di-t-butyl peroxide, t-butyl-α-cumyl peroxide, di-α-cumyl peroxide, 1,4-bis((t-butyldioxy)isopropyl) benzene, 1,3-bis((t-butyldioxy)isopropyl)benzene, 2,5-dimethyl-2,5-bis(t-butylperoxy)benzene, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane, and 2,5-dimethyl-2,5-bis(t-butylperoxy)hexene, for example.

[0032]

The following may be mentioned as peroxyketal type compounds:
1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane, n-butyl-4,4-bis(t-buylperoxy)valerate, and /6
2,2-bis(t-butylperoxy)butane, for example.

[0033]

The following may be mentioned as alkyl perester type compounds: t-butyl peroxyacetate, t-butyl peroxyisobutyrate, t-butyl peroxyoctanoate, t-butyl peroxypivalate, t-butyl peroxyneodecanoate, t-butyl

peroxy-3,5,5-trimethylhexanoate, t-butyl peroxybenzoate, t-butyl peroxylaurate, and 2,5-dimethyl-2,5-bis(benzoylperoxy)hexane, for example.

[0034]

The following may be mentioned as peroxycarbonate type compounds: bis-(2-ethylhexyl)peroxycarbonate, diisopropyl peroxycarbonate, di-sec-butyl peroxycarbonate, di-n-propyl peroxycarbonate, bis(3-methoxybutyl) peroxycarbonate, bis(2-ethoxyethyl) peroxycarbonate, bis(4-t-butylcyclohexyl)peroxycarbonate, and OO-t-butyl-O-isopropyl peroxycarbonate, for example. Succinic acid peroxide and the like may also be mentioned as other organic peroxides. These may be used alone or in mixtures of 2 or more.

[0035]

Amount of organic peroxide to be added

The amount of organic peroxide to be added depends on the type and reaction temperature, but is in the range of 0.01-5 parts by weight, preferably 0.05-3 parts by weight, more preferably 0.1-2 parts by weight, per 100 parts by weight of the higher molecular component. If it is less than 0.01 part by weight, its effect as a cross-linking agent will be insufficient. If it exceeds 5 parts by weight, the viscosity will be too high and melting and molding may be impossible.

[0036]

Flexibility

The elastic modulus of films comprising the polylactic acid-type resin composition obtained by the present invention is in the range of 50-1500. The elastic modulus/elongation of the present invention is a value obtained by a method to be described below.

[0037]

Melt tensile strength

The melt tensile strength of the polylactic acid-type resin composition obtained by the present invention is in the range of 0.7-20 g. If it is less than 0.7 g, the melt tensile strength will be unsatisfactory, so processability will be unsatisfactory. If it is greater than 20 g, there may be cases where the melt molding conversely becomes difficult. The melt tensile strength of the present invention is a value obtained by a method to be described below.

[0038]

Melt kneading

In the present invention, polylactic acid, aliphatic polyester, and an organic peroxide are blended together, subjected to melt kneading in a melt kneader, and caused to react together.

[0039]

Melt kneading temperature

In the present invention, the melt kneading temperature depends upon the type of aliphatic polyester used, the composition ratio of polylactic acid and aliphatic polyester, and the type and amount of organic

peroxide that is added, but ordinarily it will be in the range of 150-250°C, preferably 160-230°C, most preferably 170-200°C. If it is below 150°C, the resin will not melt and kneading will be impossible. If it exceeds 250°C, the resin will decompose, and the molecular weight may decline greatly in some cases, and a gel will be formed without the reaction having proceeded in other cases.

[0040]

Melt kneading time

In the present invention, the melt kneading time depends on the melt kneader and the melt kneading temperature, but ordinarily it will be on the order of 0.01-15 min.

[0041]

Other additives

In the present invention, other additives are possible as long as the object is not impaired, such as fillers, colorants, plasticizers, ultraviolet ray absorbers, antioxidants, flame retardants, internal mold release agents, anti-static agents, surface-wetting improvers, auxiliary incinerators, pigments, and lubricants, for example.

[0042]

Manufacturing method

The polylactic acid, aliphatic polyester, organic peroxide, and other additives are premixed by using a mortar, Henschel mixer, drum blender, tumbler blender, ball mill, or ribbon blender, for example, and then subjected to melt kneading by an ordinary publicly known single-axis extruder, biaxial extruder, melt kneader, Banbury mixer, Brabender, Plastograph, hot roll, or kneader, for example. The use of a

side feeder, for example, of an extruder to supply the organic peroxide and other additives is a preferred method.

[0043]

Moisture and the like

In the present invention, in consideration of the reaction effect and the thermal stability of the resin, it is preferable to perform melt kneading with the moisture content of the resin at 1000 ppm or less.

Application examples

The following items numbered (1)-(7) may be mentioned as application examples of the invented polylactic acid-type resin composition.

(1) Molded articles that contain the polylactic acid-type resin composition.

(2) Films that contain the polylactic acid-type resin composition.

(3) Inflation films that contain the polylactic acid-type resin composition.

(4) Foams that contain the polylactic acid-type resin composition.

(5) Laminates that contain a resin layer and a substrate layer, where the laminate is one in which the aforementioned resin layer contains the polylactic acid-type resin composition.

(6) Paper laminate products that contain a resin layer and a paper layer, and where the aforementioned resin layer contains the polylactic acid-type resin composition.

(7) Aluminum laminate products that contain a resin layer and an aluminum layer, and where the aforementioned resin layer contains the polylactic acid-type resin composition.

[0044]

Molding/Processing methods and applications

There are no particular limitations on the molding/processing methods for the polylactic acid-type resin composition obtained by the present invention; specific examples include injection molding, extrusion molding, inflation molding, extrusion blow molding, expansion molding, calender molding, blow molding, balloon molding, vacuum molding, spinning, and other molding/processing methods. Said polyester may also be used, by suitable molding/processing methods, in a ball-point pen, refillable pencil, pencil, or other writing implements; stationery components, golf tees, parts for smoking golf /7
balls used in ceremonial first shots, capsules for oral medicines, carriers for anal and vaginal suppositories, carriers for medical patches applied to skin or mucous membranes, capsules for agrichemicals, capsules for fertilizers, capsules for seeds and seedlings, compost [bags], fishing reels, fishing bobbers, fishing lures, lures, buoys for fishery, decoys for hunting, shells for shotgun pellets, camping goods such as eating utensils, nails, stakes, bundling materials, anti-slip materials for use on muddy or snowy roads, blocks, disposable lunch boxes, eating utensils, containers for portable lunches and prepared side dishes sold in convenience stores, chopsticks, disposable chopsticks, forks, spoons, skewers, toothpicks, containers for instant noodles, cups for use in beverage vending machines, containers and trays for food products such as raw fish, fresh meat, fruits, tofu and prepared side dishes, standardized fish packing boxes such as are used in fish markets, bottles for milk products such as milk/yogurt/lactobacillus beverages, bottles for soft drinks such as carbonated beverages and soft drinks, bottles for alcoholic beverages such as beer and whiskey, bottles for shampoo and liquid soap, with or without dispenser mechanisms, toothpaste tubes, containers for cosmetics, containers for detergents, containers for bleaches, cooling boxes, planting pots, casings for water purifier cartridges, casings for artificial kidneys and livers and the like, materials for syringes, cushioning material for use in

transporting home electrical appliances such as television and stereo sets, cushioning material for use in transporting precision machines such as computers, printers and clocks, and cushioning material for use in transporting ceramic products such as glass and porcelain.

[0045]

Lactic acid-type resin composition

The lactic acid-type resin composition pertaining to the present invention has the characteristic of being difficult to color, in comparison to polymers in which a degradable polymeric side chain has been added to a polysaccharide. The polylactic acid-type resin composition pertaining to the present invention has the characteristic of having equivalent or higher transparency, in comparison to ordinary aliphatic polyesters. The polylactic acid-type resin composition pertaining to the present invention has the characteristic of a significantly larger melt tension, in comparison to ordinary aliphatic polyester. Therefore the molding/processing properties are significantly improved, making it possible to manufacture various types of molded articles.

[0046]

The invented polylactic acid-type resin composition may also be obtained as a polylactic acid-type resin composition having desired properties by the type and composition of the hydroxycarboxylic acid. The polyhydroxycarboxylic acid (polymeric hydroxycarboxylic acid) component, which constitutes the side chain, may be a single polymer (homopolymer) or a joint polymer (copolymer); when it is a copolymer, its mode of arrangement may be either as a random copolymer, alternating copolymer, block copolymer, or graft copolymer. There are no particular limitations on the structure of the polyhydroxycarboxylic acid that constitutes the side chain: it may be either straight or branched. The

invented polylactic acid-type resin composition has a structure in which 2 or more star-shaped polymers produced by the addition of a degradable polymeric side chain (polyhydroxycarboxylic acid) to a polyfunctional center compound (aliphatic polyvalent carboxylic acid and/or anhydride thereof having 3 or more carboxyl groups) are bound by an aliphatic polyhydric alcohol having 2 or more hydroxyl groups; this is thought to be the reason for its manifestation of high melt tension, as described above.

[0047]

Melt tension

Details of the methodology for assessment of melt tension are described, for example in *Purasuchikku Kako Jijutsu Handobukku [Handbook of Plastic Finishing Technology]* (editor: Society of Polymer Science; publisher: Nikkan Kogyo Shimbun Newspaper Publishing,1995), "(2) Melt Tension," pages 1414-1416, and *Properties of Polymers: Their Correlation With Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions, Third, Completely Revised Edition* (author: D.W. van Krevelen, publisher: Elsevier, 1990), pages 686-687.

[0048]

The melt tension is measured at the testing temperature corresponding to the actual molding temperature, and is the tension necessary for drawing a strand, which has been extruded from a melt indexer at a predetermined rate, into a predetermined thread diameter. Generally, when the melt tension is large, the bubble stability will be good for inflation molding and the draw-down during flow molding will be small. There is also the neck-in phenomenon, in which the film width for products of sheet and cast film molding is narrower than the exit width of the die, and this neck-in quantity is closely related to the melt tension. The melt tension of the invented polylactic acid-type resin composition can be

controlled as desired by selecting the numeric value for specific features of the invention. The melt tension of the invented polylactic acid-type resin composition is determined by measuring the melt flow index at 2 suitable temperatures using a load of 2160 g, then determining the temperature at which the melt flow index is 10 g/10 min, by plotting the temperature against the melt flow index, then measuring the melt tension at this temperature; it is preferred that this value be 0.7 g or higher.

[0049]

Applications of the polylactic acid-type resin composition

The invented polylactic acid-type resin composition can be suitably used as a substitute for those resins that, prior to this application, have been publicly known and/or publicly used for medical applications, for packaging food products, and for general use.

[0050]

Molding/Finishing methods for the invented polylactic acid-type resin composition

There are no particular limitations on the molding/finishing methods for the invented polylactic acid-type resin composition, but specific examples of preferred methods are injection molding, extrusion molding, inflation molding, extrusion blow molding, expansion molding, calender molding, blow molding, balloon molding, vacuum molding, spinning, and other methods; of these, inflation molding, blow molding, extrusion blow molding, expansion molding, and spinning are particularly preferred. Said lactic acid-type resin composition may also be used, by suitable molding/processing methods, in a ball-point pen, refillable pencil, pencil, or other writing implements; stationery components, golf tees, parts for smoking golf balls used in ceremonial first shots, capsules for oral medicines, carriers for anal /8

and vaginal suppositories, carriers for medical patches applied to skin or mucous membranes, capsules for agrichemicals, capsules for fertilizers, capsules for seeds and seedlings, compost [bags], fishing reels, fishing bobbers, fishing lures, lures, buoys for fishery, decoys for hunting, shells for shotgun pellets, camping goods such as eating utensils, nails, stakes, bundling materials, anti-slip materials for use on muddy or snowy roads, and blocks, for example.

[0051]

The invented lactic acid-type resin composition is also suitable for use, by suitable molding/processing methods, in disposable lunch boxes, eating utensils, containers for portable lunches and prepared side dishes sold in convenience stores, chopsticks, disposable chopsticks, forks, spoons, skewers, toothpicks, containers for instant noodles, cups for use in beverage vending machines, containers and trays for food products such as raw fish, fresh meat, fruits, tofu and prepared side dishes, standardized fish packing boxes such as are used in fish markets, bottles for milk products such as milk/yogurt/lactobacillus beverages, bottles for soft drinks such as carbonated beverages and soft drinks, bottles for alcoholic beverages such as beer and whiskey, bottles for shampoo and liquid soap, with or without dispenser mechanisms, toothpaste tubes, containers for cosmetics, containers for detergents, containers for bleaches, cooling boxes, planting pots, casings for water purifier cartridges, casings for artificial kidneys and livers and the like, materials for syringes, cushioning material for use in transporting home electrical appliances such as television and stereo sets, cushioning material for use in transporting precision machines such as computers, printers and clocks, and cushioning material for use in transporting ceramic products such as glass and porcelain.

[0052]

Production and manufacture of films and sheets

The invented lactic acid-type resin composition is suitable for finishing when strength is required of a melted polymer, such as blow molding, foam molding, and extrusion molding, for example. In the case of a sheet produced by extrusion molding, for example, it has the characteristic that the decrease in sheet width due to neck-in or drooping of the melted sheet is small.

(1) Manufacturing technology

Films and sheets containing the invented lactic acid-type resin composition can be manufactured by technologies such as publicly known and/or publicly used extrusion methods, co-extrusion methods, calender methods, hot press methods, solvent casting methods, inflation methods, balloon methods, and tenter methods, for example. The manufacturing conditions should be established in consideration of the thermal properties, molecular structure, and crystal properties, for example, of the lactic acid-type resin composition to be supplied for manufacturing.

[0053]

(2) Additives

It is possible to manufacture films and sheets containing the invented lactic acid-type resin composition to have certain desired properties, gas barrier properties, optical properties, transparent optical wavelength spectrum, opacity, oil resistance, and other properties, by suitable selection, according to the objective, of extrusion conditions, extension conditions, and additives (for example, antioxidants, thermal stabilizers, ultraviolet ray stabilizers, lubricants, fillers, adhesion preventors,

anti-static agents, surface wetting improvers, auxiliary incinerators, anti-slip agents, and pigments), for example.

(3) Process design

In the manufacturing process, it is possible to appropriately establish, according to the objective, conditions such as the monoaxial extension rate, biaxial extension rate, number of extension steps, heat treatment temperature, rate of change in the heat treatment temperature, number of cooling rollers, disposition and mode of cooling rollers, wind-up mode onto cooling rollers, temperature of cooling rollers, degree of mirror finish on the cooling roller surface, and the like.

[0054]

(4) Methodology for quality control

In the manufacturing process, it is possible to implement quality control by manual or automatic control of variations in product thickness by detection of product thickness data by using publicly known and/or publicly used optical measurement methods, using radiation, magnetic waves, light, or ultrasound, and then feeding this data back into the manufacturing process. Examples of optical measurement methods that use radiation include transmission type (absorption type) and scattering type alpha ray thickness meters, beta ray thickness meters, and gamma ray thickness meters; publicly known and/or publicly used radioisotopes may be used as the source of radiation.

[0055]

Methodology of the post-treatment process and finishing process

With regard to the posttreatment process and finishing process, it is possible to conduct the following posttreatment processes and finishing processes: welding, heat sealing, perforating, primer coating, adhesive coating, medicinal coating, parkerizing, evaporation, sputtering, CVD, coating, etching, spraying, staining, painting, electrostatic coating, airbrushing, laminating, sandwiching, embossing, relief engraving, stamping, corrugation, printing, transferring, sanding, sand blasting, shirring, punching, making honeycomb structures, making corrugated fiberboard structures, and making a multilayered structure.

[0056]

(6) Methodology of the extrusion method and co-extrusion method

With regards to the extrusion method and co-extrusion method, it is possible to use publicly known and/or publicly used methods such as the T-die, inflation die (round die), flat die, feed block/single manifold die or single manifold that combines multiple feed blocks, and the like. With regard to the co-extrusion method, it is possible to manufacture multilayer films by using multiple said polymers having different properties and/or other polymers. The use of the inflation method or balloon method makes it possible to relatively inexpensively manufacture, with high produceability, robust products that have low coefficient of extension, and/or high elastic modulus, and/or high toughness, because biaxial simultaneous extension is possible. And, because the shape is bag-like (seamless shape), it is highly suitable for the production of bags, such as compost bags, supermarket bags, and bags for protection /9
against moistening of surroundings by water condensing on food product bags for low temperatures such as for frozen foods and fresh meats, for example. By combination with the co-extrusion method, it is

possible to manufacture multilayered films with high productivity, using multiple lactic acid-type resin compositions of the invention having different properties and/or other polymers. It is also possible to combine the inflation method or the balloon method with the co-extrusion method. It is possible for films or sheets containing the invented lactic acid-type resin composition to be manufactured into roll shapes, tape shapes, cut sheet shapes, plate shapes, or bag shapes (seamless shapes), by establishing the processing conditions according to the objective.

[0057]

(7) Secondary finishing

Films or sheets containing the invented lactic acid-type resin composition can manifest properties that are difficult to satisfy by polyhydroxycarboxylic acid alone. For example, the draw-down of polyhydroxycarboxylic acid by itself is large, so the margin for selecting molding/finishing conditions such as processing temperature and molding cycles is relatively narrow. In contrast, the draw-down is small for the invented lactic acid-type resin composition, so the margin for selecting molding/finishing conditions such as processing temperature and molding cycles is relatively wide. Therefore films or sheets containing the invented lactic acid-type resin composition can be given two-, three-, or higher-dimensional shapes such as elongation processing, blow processing, or vacuum molding, for example, and thus they are suitable materials for secondary processing.

[0058]

(8) Specific examples of applications

Films or sheets containing the invented lactic acid-type resin composition can be used for shopping bags, garbage bags, compost bags, cement bags, fertilizer bags, foodstuff and confectionery wrapping

films, food-wrapping films, films for agriculture and horticulture, films for hot houses, packaging films for magnetic tape cassettes such as for video or audio, floppy disk packaging films, fences, oil fences for marine or riverine or lake and wetland use, adhesive tapes, tapes, bundling materials, waterproof sheets, umbrellas, tents, sandbags, cement bags [sic], and fertilizer bags [sic], for example. It is also possible to make porous films that are permeable to air by performing an additional elongation process on films prepared by extrusion of polymers containing inorganics such as calcium carbonate, barium sulfate, or titanium oxide, and these films can be used for diaper covers or for special packaging materials, for example.

[0059]

Manufacture of seamless pipes

It is possible to manufacture seamless pipes containing the invented lactic acid-type resin composition by extrusion using round dies. By combining this with the co-extrustion method, and by using multiple lactic acid-type resin compositions of the invention having different properties, or by using some other type of polymer, it is possible to manufacture multilayered seamless pipes.

[0060]

The manufacture of square materials and/or round materials

It is possible to manufacture square materials and/or round materials containing the invented lactic acid-type resin composition by extrusion using dies. By using multiple lactic acid-type resin compositions of the invention having different properties, or by using some other type of polymer, it is possible to manufacture multilayered square materials or round materials. By combining this with the co-extrusion method, it is possible to manufacture multilayered square materials or round materials

having specific cross-sectional structures and cross-sectional profiles, such as the "Kintaro" shape of traditional Japanese candy, a coiled shape, or the shape of a specially wrapped Japanese omelet.

[0061]

Foam

(1) The concept of the word "foam"

The concept of the word "foam" that has already been used in the Claims and Detailed Description of the present application includes a resin structure that has a 2-phase or multiphase structure, having a mixture of void phases (including continuous voids and independent voids) of small apparent density within the continuous phase of the resin, there being present many spaces (including air pockets, voids, microvoids, and cavities) within the resin; it includes in general anything recognized having a structure such as, for example, high molecules having a cell structure, foaming high molecules, swelling high molecules, and high molecular foams, and it also includes soft things as well as hard things.

[0062]

(2) Manufacture of the foam

It is possible to manufacture a foam that contains the invented lactic acid-type resin composition according to publicly known and/or publicly used methods. It is suitable to use, for example, the foaming agents and foaming techniques described on pages 811-815 of *The Maruzen Polymer Dictionary - Concise Encyclopedia of Polymer Science and Engineering* (edited by Kroschwitz, translated by Mita, published by Maruzen, Tokyo, 1994). It is also possible, suitably, to use novel or publicly known and/or publicly used foaming agents and foaming techniques that meet environmental regulation standards according to the regulations of the Montreal Protocol concerning

chlorofluorocarbon regulation in order to protect the ozone layer. It is possible to control the properties of the spaces (including air pockets, voids, microvoids, and cavities), such as continuous, independent, size, shape, distribution, and homogeneity of size, of the foam, suitably, according to the objective, by establishing the foaming conditions.

[0063]

(3) Foaming agents

Foaming agents include: inert gases, chemical foaming agents that produce inert gases when they decompose, hydrocarbons or chlorinated hydrocarbons that have 3-5 carbon atoms, fluorocarbons, chlorofluorocarbons, water, nitrogen, LPG, LNG, low boiling point organic liquids, carbon dioxide gas, and inert gases [sic], for example. The following may be mentioned as chemical foaming agents: sodium hydrogen carbonate, dinitrosopentamethylene tetramine, sulfonyl hydrazide, azodicarbonamide, p-toluene sulfonylsemicarbazide, 5-phenyltetrazole, diisopropyl hydrazodicarboxylaze [sic], 5-phenyl-3,6-dihydro-1,3,4-oxadiazin-2-one, and sodium borohydroxide, for example. The following may be mentioned as physical foaming agents: pentanes such as n-pentane, 2,2-dimethyl propane, and 1-pentene; hexanes such as n-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and cyclohexane; heptanes such as n-heptane, 2,2-dimethylpentane, 2,4-dimethylpentane, 3-ethylpentane, /10
and 1-heptene; toluene, trichloromethane, tetrachloromethane, trichlorofluoromethane, methanol, 2-propanol, isopropyl ether, and methylethyl ketone, for example. The following may be mentioned as examples of fluorocarbons: chlorofluorocarbons of the CFC series such as CFC-11, CFC-12, CFC-113, and CFC-114, for example.

[0064]

(4) Applications for general use

The foam that contains the invented lactic acid-type resin composition is also suitable for use, for example, in disposable lunch boxes, eating utensils, containers for portable lunches and prepared side dishes sold in convenience stores, containers for instant noodles, cups for use in beverage vending machines, containers and trays for food products such as raw fish, fresh meat, fruits, tofu and prepared side dishes, standardized fish packing boxes such as are used in fish markets, containers for milk products such as milk/yogurt/lactobacillus beverages, containers for soft drinks such as carbonated beverages and soft drinks, containers for alcoholic beverages such as beer and whiskey, containers for cosmetics, containers for detergents, containers for bleaches, cooling boxes, planting pots, tapes, cushioning material for use in transporting home electrical appliances such as television and stereo sets, cushioning material for use in transporting precision machines such as computers, printers and clocks, cushioning material for use in transporting optical machines such as cameras, lenses, microscopes, and telescopes, cushioning material for use in transporting ceramic products such as glass and porcelain, shading material, heat-insulating material, and soundproofing material.

[0065]

(5) Medical applications and sanitation applications

The foam that contains the invented lactic acid-type resin composition is also suitable for use, for example, in medical applications and sanitation applications; specific examples include dressings, carriers for medical patches applied to skin or mucous membrane, triangular bandages, adhesive plasters, towels, disposable towels, heatable towels, rags, tissues, wet tissues for cleaning and disinfecting, tissues for wiping baby's buttocks, disposable diapers, napkins for sanitary and secretion uses, sanitary tampons,

blood-absorbing tampons for surgical and maternity uses, sanitary cover stock materials and sterilizing bags. These medical and sanitary products can be sterilized, subjected to sterilization, or disinfected by publicly known and/or publicly used techniques using sterilization by heating or steam, sterilization by ethylene oxide gas, sterilization by hydrogen peroxide water or ozone, sterilization by irradiation of ultraviolet rays or electromagnetic waves, sterilization by irradiation of gamma rays or other radiation, sterilization by ethanol or benzalkonium chloride, for example, and then subjected to sterile packaging. It is also possible to manufacture and package the product in a sterile condition or endotoxin-free condition by establishing processes in clean rooms or clean benches where it is possible to supply a laminar flow of ultrapurified air by a HEPA filter.

[0066]

(6) General industrial and recreational applications

Furthermore, the foam that contains the invented lactic acid-type resin composition is also suitable for use, for example, in general industrial applications including agriculture, fishery, forestry, industry, civil engineering and traffic, as well as recreational applications including leisure and sports. For example, it can be used suitably as agricultural cheesecloth, oil-absorbing materials, soft/weak ground-reinforcing materials, artificial leathers, substrate for floppy disks, sand bags, heat-insulating materials, soundproofing materials, cushioning materials, cushioning materials for furniture such as beds and chairs, floor cushioning materials, packaging materials, bundling materials, and anti-slip materials for use on muddy or snowy roads.

[0067]

Spun thread

(1) The concept of the word "thread" that has already been used in the Claims and Detailed Description of the present application includes the concept of "raw thread" described on pages 393-421 of *Seni Binran: Kakohen [Fiber Compendium: Volume on Processing]* (edited by Seni Gakkai [Society of Fiber Science and Technology], Maruzen, Tokyo, 1969); it includes, for example, monofilaments, multifilaments, staple fibers (s.f.), tow, high bulk staple fibers, high bulk tow, spun yarn, union yarn, processed yarn, textured yarn, modified cross-section yarn, hollow yarn, conjugate yarn, POY (partially oriented yarn), DTY (drawn textured yarn), POY-DTY, and sliver.

[0068]

(2) Manufacture of thread (spinning, filature)

The invented lactic acid-type resin composition is a suitable material for melt spinning and dry spinning. The invented lactic acid-type resin composition can be finished into threads and textiles that have properties or characteristics such as desirable thickness, cross-sectional shape, fineness (tex, denier, yarn count, for example), twist, tensile strength and strain under tension, tying strength, heat resistance, crimp degree, water absorption, oil absorption, bulking power, drape, and feeling, by suitably setting yarn-making conditions, spinning conditions, textile conditions, posttreatment conditions, dyeing conditions and other processing conditions.

[0069]

(3) Manufacture of yarns with non-standard cross-sections and/or multilayered structures and/or hollow yarns and the like

By setting the spinning nozzle suitably, according to the purpose, the invented lactic acid-type resin composition can be suitably spun in fibers having polygonal crosssections or non-standard shapes represented by silk having a triangular cross-sectional structure, fibers having a conjugate structure that resembles the bilateral structure of sheep's wool, fibers having a core/shell structure that resembles the cuticle/cortex/medulla coaxial 3-layer structure of sheep's wool, or fibers having a hollow structure that resembles the lumen structure of cotton. By spinning with a multilayered head (nozzle, orifice), it is possible to manufacture thread having multilayered structure crosssections, using either the invented lactic acid-type resin compositions having different properties, or other types of polymer. By combining this type of co-spinning, it is possible to manufacture yarns having specific cross-sectional structures and cross-sectional profiles, such as the "Kintaro" shape of traditional Japanese candy, a coiled shape, the shape of a specially wrapped Japanese omelet, or a tree-ring shape typical of German Baumkuchen, for example.

[0070]

It is possible to manufacture hollow fibers that contain the invented lactic acid-type resin composition by spinning with a hollow head (nozzle, orifice). By combining this with co-spinning, it is possible to manufacture multilayered hollow fibers using either the invented lactic acid-type resin compositions having different properties, or other types of polymer. For example, it may be applied to /11
textiles that have the spaces of their hollow fibers filled with pigment so they are not transparent even when wetted with water, or applied to textiles that have the spaces of their hollow fibers filled with liquid crystals so they change color tone according to temperature, or applied to head-absorbing textiles that have the spaces of their hollow fibers filled with ceramics or carbon black so they absorb far

infrared radiation, or applied to fishing nets that have the spaces of their hollow fibers filled with lead so that they sink into the water.

[0071]

(4) Process design

It is possible, suitably, according to the purpose, with regard to the filature process, to establish conditions such as spinning nozzle shape/mode, draw ratio, number of drawing steps, heat treatment temperature, rate of change in the heat treatment temperature, crimp distribution, and oil agent treatment, for example.

(5) Products

It is possible to suitably manufacture filaments that contain the invented lactic acid-type resin composition having the desired degree of fineness, from ultrafine fibers that rival the fibers structured by Ecsaine (Toray) or fibers that are even finer than that, to ultrathick fibers that rival the thickness of industrial fibers for fasteners, or fibers that are even thicker than that.

[0072]

The manufacture of textiles

(1) The concept of the word "textile"

The concept of the word "textile" that has already been used in the Claims and Detailed Description of the present application generally includes anything that is recognized as having a fibrous structure such as woven fabrics, knit fabrics, nonwoven fabrics, braids that include string and rope, cottony high bulk staple fiber, sliver, porous sponge, felt, paper, and nets, for example.

(2) Manufacture of textiles

It is possible to manufacture filament yarn textiles, spun yarn textiles, stretch textiles, and textiles for industrial materials by the use of publicly known and/or publicly used looms or shuttleless looms (water jet looms, air jet looms).

[0073]

(3) Manufacture of knits, braids, nets, and the like

It is possible to manufacture, using publicly known and/or publicly used knitting machines, knits, flat knits, round knits, warp knits, tricots, round knit stockings, seamless stockings, tricot stockings, laces, braids, and nets.

(4) Manufacture of S.F. (staple fibers)

It is also possible for staple fibers containing the invented lactic acid-type resin composition to be co-spun by any staple diagram and with any mixture of staple fibers of other natural fibers, synthetic fibers, and/or semisynthetic fibers. It is possible to suitably use staple fibers containing the invented lactic acid-type resin composition as raw materials for paper, as filler for composite materials, as whiskers (cat whiskers) for composite materials, or as fibers for FRP filler.

[0074]

(5) Manufacture of nonwoven fabric

It is possible to manufacture nonwoven fabrics containing the invented lactic acid-type resin composition by publicly known and/or publicly used techniques. For example, in the manufacture of a

nonwoven fabric containing the invented lactic acid-type resin composition, it is possible to suitably use the manufacturing method described on pages 906-910 of *The Maruzen Polymer Dictionary - Concise Encyclopedia of Polymer Science and Engineering* (edited by Kroschwitz, translated by Mita, published by Maruzen, Tokyo, 1994). In the manufacture of a nonwoven fabric containing the invented lactic acid-type resin composition, it is possible to suitably use, for example, the dry card method, the heat bonding method, air array method, wet method, spun bond method, melt blow method, microfiber method, flowing water interlacing method, needle punch method, cumulative layer method, stitch bond method, or paper-making method, for example. Nonwoven fabrics containing the invented lactic acid-type resin composition, similar to commercially available nonwoven fabrics such as Thinsulate (registered trademark of 3M) or Eizac (registered trademark of Teijin), resembling Gortex (registered trademark, Junkosha Inc., extension microporous polytetrafluoroethylene (PTFE)) or Espoaaru (registered trademark, Mitsui Toatsu), which permit passage of steam, can be used to winterize and/or waterproof clothing (alpineering, skiing, and similar applications) by being combined with waterproof sheets that do not permit the passage of water.

[0075]

(6) Uses of textiles

Textiles that contain the invented lactic acid-type resin composition may be used for general clothing or medical clothing outer garments, industrial clothing, surgical garb, nightgowns, undergarments, underclothes, back fabric, hats, masks, sashes, triangular bandages, socks, lady's stockings, lady's foundation (brassieres or shorts for example), pantyhose, tights, stockings, military socks, towels, gauze, hand towels, carpets, mats, curtains, wallpaper, clothing cores, automobile inner trim, mattresses, bags, wrapping cloths, bedclothes, bed quilt cotton, pillow covers, blankets, sheets, heat-insulating materials

for winter clothes, lace, tape, synthetic/artificial hide, synthetic/artificial fur, synthetic/artificial suede, a synthetic/artificial leather and network pipes. Also, the textiles that contain the invented lactic acid-type resin composition are suitable for medical or sanitary purposes. For example, the textiles can be suitably used in sutures for surgical operations, bandages, triangular bandages, adhesive plasters, towels, disposable towels, disposable wet towels, roll towels for business, heatable towels, rags, tissues, wet tissues for cleaning and disinfecting, tissues for wiping baby's buttocks, disposable diapers, disinfecting cotton, napkins for sanitary and secretion uses, sanitary tampons, underpads, blood-absorbing tampons for surgical and maternity uses, sanitary cover stock materials, sterilizing bags, nets for holding kitchen garbage, and trash bags. These medical and sanitary products can be sterilized, subjected to sterilization, or disinfected, and also packaged in sterile fashion, by methods identical to those for the foam products described above. They may also be manufactured and packaged in a sterile condition or endotoxin-free condition by methods identical to those for the foam products described above.

[0076]

The textiles that contain the invented lactic acid-type resin composition can be suitably used for general industrial applications including agriculture, fishery, forestry, manufacturing, construction and civil engineering, transportation and traffic, as well as recreational applications including leisure and sports. For example, they can be used suitably as agricultural cheese cloths, nets against insects and /12
birds, sieves, fishing lines, fishing nets, casting nets, spreading nets, oil-absorbent materials, nets, ropes, climbing ropes, sails (nautical), hoods, tarpaulins, plastics for wrapping shipping pallets, container bags, industrial transit bags, cement bags, fertilizer bags, filter materials, water-permeable cloths for reclamation, soft/weak ground reinforcing materials, artificial leather, felt for paper making, substrate for floppy disks, tents, sand bags, planting nets, heat-insulating materials, soundproofing materials,

shade materials, shock cushioning materials, cushion materials, bundling materials, anti-slip materials for use in muddy or snowy roads, network pipes, and drainage pipes for civil engineering and construction, for example. The aforementioned "shock cushioning materials" include cushioning material for use in transporting home electrical appliances such as television and stereo sets, cushioning material for use in transporting precision machines such as computers, printers and clocks, cushioning material for use in transporting optical machines such as cameras, lenses, microscopes, and telescopes, and cushioning material for use in transporting ceramic products such as glass and porcelain.

[0077]

Application examples

The following statements explain the invention more specifically with reference to application examples, but the invention is not limited to these examples, as long as the technical scope of the invention is not exceeded. The following methods were used for measurement of weight average molecular weight (Mw) of the polylactic acid type resin, and the melt tension (MT value) and flexibility (elongation) in the application examples.

[0078]

(1) Weight average molecular weight (Mw)

This was measured by gel permeation chromatography (GPC) with polystyrene as the reference. The measurement conditions are described below.

GPC: Shodex System 11 (Showa Denko)

Column used: K-805L x 2, K-800P (precolumn)

Column temperature: 40°C

Solvent: chloroform

Flow rate: 1.0 mL/min

Sample concentration: 3 mg/1 mL

Test charge: 100 μm

[0079]

(2) Melt tension (MT value)

The melt flow index is measured at 2 suitable temperatures using a load of 2160 g, then a determination is made, by plotting the temperature against the melt flow index, of the temperature at which the melt flow index is 10 g/10 min, and this temperature is used for measuring the melt tension. The methodology is described, for example in *Purasuchikku Kako Jijutsu Handobukku [Handbook of Plastic Finishing Technology]* (editor: Society of Polymer Science; publisher: Nikkan Kogyo Shimbun Newspaper Publishing), pages 1414-1416, and *Properties of Polymers: Their Correlation With Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions, Third, Completely Revised Edition* (author: D.W. van Krevelen, publisher: Elsevier, 1990), pages 686-687.

[0080]

(3) Flexibility, elongation

A pressed film having a thickness of 100 μm (±5) was manufactured by hot pressing the obtained polylactic acid-type resin composition. The method described in JIS K6732 was used to punch sample shapes for tensile shearing load and elongation tests from the pressed film. These test samples were then

used to conduct tension tests using a Strograph M. The elongation was calculated using the following formula.

[Formula 1]

Elongation (%) = distance between benchmarks after testing/distance between benchmarks before testing

The test conditions were as follows.

Distance between chucks: 7 cm

Distance between benchmarks: 4 cm

Tension rate: 200 mm/min

[0081]

Manufacturing Example 1

400 g of L-lactide, 0.04 g of stannous octanoate, and 0.12 g of lauryl alcohol were charged into a thick-walled cylindrical stainless polymerization reactor equipped with a stirrer, and degassed for 2 h in vacuum. After nitrogen gas exchange, this was heated at 200°C/10 mm Hg for 2 h while stirring. After the reaction, a melt of polylactic acid was taken out of the outlet mouth at the bottom, cooled in air, and cut with a pelletizer. The amount of obtained polylactic acid was 340 g, for a yield of 85%, and the weight average molecular weight (Mw) was 138,000. The melt tension was 0.6 g.

[0082]

Manufacturing Example 2

10 kg of 90% L-lactic acid and 45 g of tin powder were charged into a reactor equipped with a Dien-Stark trap, and heated at 150°C/50 mm Hg for 3 h while stirring as water was distilled out, and

then this was further stirred for another 2 h at 150°C/30 mm Hg for oligomerization. 21.1 kg of diphenyl ether was added to the oligomer and this was reacted at 150°C/35 mm Hg for azeotropic dehydration; the distilled water and solvent were separated, and only the solvent was returned to the reactor. After 2 h, the organic solvent to be returned to the reactor was passed through a column filled with 4.6 kg of Molecular Sieve 3A and then returned to the reactor, where it underwent reaction for 20 h at 130°C mm Hg, giving a polylactic acid solution having a weight average molecular weight (Mw) of 150,000. The solution was diluted by addition of 44 kg of dehydrated diphenyl ether, then cooled to 40°C, and the precipitated crystal was filtered. Then 12 kg of 0.5N HC1 and 12 kg of ethanol were added to the crystal, this was stirred at 35°C for 1 h, and then filtered. This was dried at 60°C/50 mm Hg, giving 6.1 kg of polylactic acid powder (yield, 85%). The powder was melted in an extruder and pelletized, giving polylactic acid. This polymer had a weight average molecular weight (Mw) of 147,000 and a melt tension of 0.6 g.

[0083] /13

Manufacturing Example 3

A reaction was conducted identical in method to that of Manufacturing Example 2, with the exception that 10 kg of 6-hydroxycaproic acid were used instead of L-lactic acid, giving 7.1 kg of polycaprolactone powder (yield: 82%). The weight average molecular weight (Mw) was 150,000. The melt tension was 0.7 g.

[0084]

Manufacturing Example 4

A reaction was conducted identical in method to that of Manufacturing Example 2, with the exception that 4.33 kg of 1,4-butanediol were used instead of L-lactic acid, giving 6.6 kg of polycaprolactone powder (yield: 80%). The weight average molecular weight (Mw) was 141,000. The melt tension was 0.6 g.

[0085]

Application Examples 1-6

Comparative Examples 1-5

As shown in Table 1, the polylactic acid obtained by Manufacturing Example 1 and/or 2 was mixed with aliphatic polyester and organic peroxide using a Henschel mixer, this was subjected to melt kneading using a single-axis extruder, and this was then pelletized. The cylinder temperature was 170-200°C. Measurements were taken of the weight average molecular weight (Mw), melt flow index, and melt tension of the obtained resins. The pellets were subjected to hot pressing in a pressing apparatus within a temperature range of 190-200°C to form a pressed film having a film thickness of 100 μm (±5 μm). Tension test sample shapes were punched from the obtained film and elongation was measured. The results are shown in Table 1.

[0086]

Raw materials used in the application examples

PLA 1: polylactic acid of Manufacturing Example 1 Mw 138,000

PLA 2: polylactic acid of Manufacturing Example 2 Mw 147,000

PCL 1: polycaprolactone of Manufacturing Example 3 — Mw 150,000

PCL 2: Celgreen PH7 (tradename of Daicel Chemical Industries) — Mw 70,000

PSB 1: polybutylene succinate of Manufacturing Example 4 — Mw 141,000

PSB 2: Bionole#1020 (tradename of Showa Polymer) — Mw 105,000

[0087]

Table 1: Application Examples 1-6

実施例	(A) 成分；高分子成分 (a−1) ポリ乳酸 [重量部]	(A) 成分；高分子成分 (a−2) 脂肪族ポリエステル [重量部]	(B) 成分；有機過酸化物 [重量部]	溶融張力 [g]	弾性率 [MPa]	伸び [%]
1	PLA1 100重量部	PCL1 50重量部	PO−1 0.5重量部	8.2	1200	230
2	PLA2 100重量部	PCL1 100重量部	PO−1 0.5重量部	11	1000	300
3	PLA2 100重量部	PCL2 100重量部	PO−1 0.5重量部	12	1000	260
4	PLA2 100重量部	PSB1 100重量部	PO−1 0.5重量部	18	850	350
5	PLA2 100重量部	PSB2 30重量部	PO−1 0.5重量部	2.5	1500	200
6	PLA2 100重量部	PSB1 100重量部	PO−1 0.1重量部	0.8	880	210

凡例：PO−1；1，3−ビス（（t−ブチルジオキシ）イソプロピル）ベンゼン（パーブチルP）

PO−2：2，6−ジメチル−2，5−ビス（t−ブチルパーオキシ）ヘキサン

（B）成分の有機過酸化物の重量部は、（A）成分の高分子成分１００重量部に対する数値.

Key: 1 Application Example

2 Ingredient (A): Polymer Ingredients

3 (a-1) Polylactic acid (parts by weight)

4 (a-2) Aliphatic polyester (parts by weight)

5 Ingredient (B): organic peroxide (parts by weight)

6 Melt tension

7 Elastic modulus

8 Elongation

9 Parts by weight

10 Example expansion: PO-1: 1,3-bis((t-butyldioxy)isopropyl)benzene (perbutyl P)

Example expansion: PO-2: 6-dimethyl-2,5-bis(t-butylperoxy)hexane

The numeric value for parts by weight of Ingredient (B), the organic peroxide, is expressed as against 100 parts by weight of Ingredient (A), the polymer ingredient.

[0088]

Table 2: Comparative Examples 1-6

比較例	（Ａ）成分；高分子成分		（Ｂ）成分：有機過酸化物［重量部］	溶融張力［ｇ］	弾性率［ＭＰａ］	伸び［％］
	（ａ－１）ﾎﾟﾘ乳酸［重量部］	（ａ－２）脂肪族ﾎﾟﾘｴｽﾃﾙ［重量部］				
１	ＰＬＡ２ １００重量部	ＰＣＬ２ １００重量部	なし	０．６	１０００	９０
２	ＰＬＡ２ １００重量部	ＰＳＢ２ １００重量部	なし	０．６	１３００	１２０
３	ＰＬＡ２ １００重量部	なし	ＰＯ－１ 0.5重量部	５．０	２０００	１０
４	ＰＬＡ２ １００重量部	ＰＣＬ２ １００重量部	ＰＯ－１ ６重量部	ｹﾞﾙ化 測定不能	ｹﾞﾙ化 測定不能	ｹﾞﾙ化 測定不能
５	ＰＬＡ２ １００重量部	ＰＳＢ２ １００重量部	ＰＯ－１ ６重量部	ｹﾞﾙ化 測定不能	ｹﾞﾙ化 測定不能	ｹﾞﾙ化 測定不能

Example expansion: PO-1: 1,3-bis((t-butyldioxy)isopropyl)benzene (perbutyl P)

PO-2: 2,6-dimethyl-2,5-bis(t-butylperoxy)hexane

The numeric value for parts by weight of Ingredient (B), the organic peroxide, is expressed relative to 100 parts by weight of Ingredient (A), the polymer ingredient.

Key:
1 Comparative Example
2 Ingredient (A): Polymer Ingredients
3 (a-1) Polylactic acid (parts by weight)
4 (a-2) Aliphatic polyester (parts by weight)
5 Ingredient (B): organic peroxide (parts by weight)

6 Melt tension

7 Elastic modulus

8 Elongation

9 Parts by weight

10 None

11 Unable to measure gelation

[0089]

Effect of the Invention

The polylactic acid-type resin composition obtained by the present invention has improved flexibility and melt tensile strength. It is also a method that can obtain it in a short period of time by an extruder.